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Investigation of Ternary Transition-Metal Nitride Systems by Reactive Cosputtering

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A reactive dc cosputtering technique has been used to evaluate compound formation in bimetallic transition-metal nitride systems. A wide range in M–M′ composition can be studied in a single deposition run, and the method is applicable to nonalloying metal combinations. Using this technique, it was found that δ-NbN and YN form a continuous (Nb,Y)N solid solution of the NaCl type, in which the superconducting transition temperature varies with the Nb:Y ratio. In the Gd–Cr–N system only limited solid solubility of CrN and GdN was found, and evidence was obtained for a new Gd–Cr–N species centered around the $GdCr_2$ composition. This species shows a low-temperature magnetic transition.

Introduction

Transition-metal nitrides display a wide spectrum of interesting physical properties that make them useful materials for a variety of different purposes. These range from coatings of high mechanical hardness and specular nature (TiN) to superconducting materials with high critical current density (δ-NbN) and magnetic materials (e.g., Fe_4N).[1] Ternary transition-metal-containing nitrides are of interest as they should make a wider range of nitride structure types available, in which the electronic and magnetic properties can be more finely tuned. This can be done extensively in transition metal oxide systems. Unfortunately these ternary species are exceedingly difficult to synthesize, partly due to the highly refractory nature of transition-metal nitrides. Although in recent years interesting progress has been made in the synthesis of ternary species using reactive nitrides such as Li_3N and M_3N_2 (M = Ca, Sr, Ba),[2] the most frequently used method is the nitriding of binary alloys. This method often yields relatively nitrogen-poor phases of the interstitial nitride/carbide type. It is also not as readily applicable to metal combinations that do not form binary alloys. Here we describe a method using reactive dc cosputtering of two metals to evaluate compound formation in M–M′–N systems in a relatively simple manner. The technique is applicable to nonalloying metal combinations. This approach is used to study the previously unexplored Y–Nb–N and Gd–Cr–N systems, providing evidence for a new superconducting (Nb,Y)N solid solution and a new Cr:Gd = 2:1 nitride species.

Experimental Section

Thin films of binary transition-metal nitrides have been successfully produced by a number of reactive sputtering techniques. Especially reactive dc sputtering (using N_2/Ar sputtering gas) allows deposition of nitride films at low substrate temperatures.[3] The combination of high surface mobility and low bulk diffusion (the substrate temperature being much lower than the temperatures used in bulk nitriding reactions) enables the formation of metastable phases, e.g., superconducting δ-NbN.[4] In our investigations the reactive sputtering conditions for one type of binary nitride for each of the metals are optimized separately, followed by a simultaneous reactive cosputtering deposition using the setup as described below. This technique has previously been used in our lab to investigate the psudobinary Gd–Y–N solid solution system.[5]

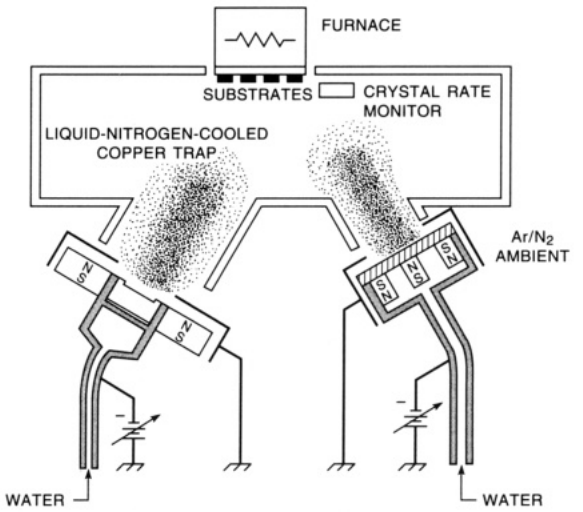

Figure 1. Representation of the geometry of the two sputtering guns, sample substrates, and copper trap as used in the reactive cosputtering experiments. The substrate heater and a third sputtering gun used to deposit the AlN protective overlayer are not shown.

The experimental setup used consists of a vacuum chamber equipped with two dc sputtering guns positioned relative to the substrate holder and heater assembly as shown in Figure 1. A series of nine 1 × 1 × 0.05 cm amorphous silica substrates was placed in fixed positions along the line between the sputtering

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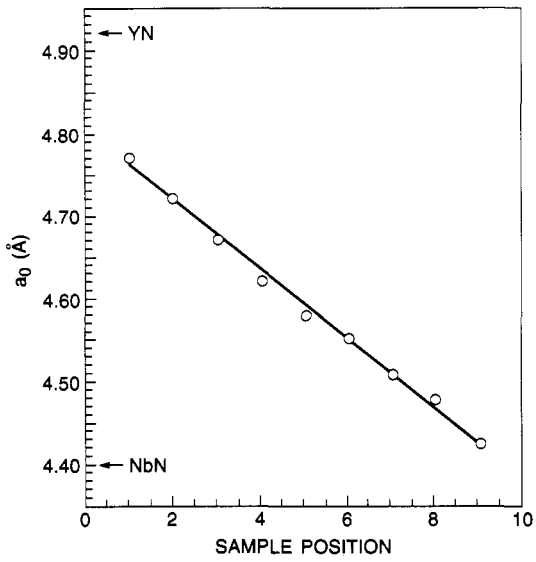

Figure 2. Plot of observed cell parameters versus sample position (see ref 7) for cubic (Nb,Y)N films.

guns. A third gun, out of the plane of the figure, is used to provide a 100–200-Å protective layer of AlN for moisture-sensitive films. By independently controlling the deposition rate from each gun a smooth linear M–M′ compositional gradient for the two sputtered metals can be obtained across the substrates. The film deposition rates used were on average 100 Å/min. The sputtering gas used is N_2/Ar, and the total pressure and N_2 partial pressure may be varied. The sputtering is performed in a copper enclosure cooled by liquid nitrogen, which results in an extremely low background pressure and oxygen and other reactive species (typically $<2 \times 10^{-10}$ Torr effective pressure of reactive species during sputtering; this is crucial to prevent contamination of oxygen-sensitive films).[6] Substrates may also be replaced by carbon grids to prepare samples for electron microscopy. This technique allows investigation of M–M′–N systems over a significant spread in M–M′ composition in a single deposition run.

The thin films were found to be very air sensitive; to avoid degradation, we deposited a thin (~100 Å) layer of AlN on the top surface of the film in situ as soon as the substrates cooled to below 200 °C and stored the samples in a desiccator. This procedure prevents measurable oxidation and hydrolysis and does not interfere with structural measurements. Small indium contacts soldered to the top surface yielded reliable low-resistance connections to the sample—presumably the act of soldering breaks through the AlN layer locally, since metal pads (such as Ag or Au) deposited on the AlN layer typically make poor contacts.

Results and Discussion

(Nb,Y)N. Reactive cosputtering of Nb and Y was performed at 9 mTorr (1.2 Pa) 20 mol % N_2 in Ar as the sputtering gas and a substrate temperature of 750 °C. Under these conditions sputtering of the individual metals gave smooth films of the cubic NaCl-type nitrides δ-NbN and YN, respectively. X-ray diffraction on the Nb–Y–N films indicated formation of a full (Nb,Y)N solid solution of the NaCl type over the compositional range studied. Cell constants calculated from the diffraction patterns suggest a linear dependence of cell constant with composition, i.e., position in the phase spread (Figure 2). The composition of the films could not be measured directly using either Rutherford backscattering or X-ray fluorescence due to the proximity of Nb and Y in the periodic table. Experience with systems that do allow RBS analysis showed that a good linear compositional gradient is

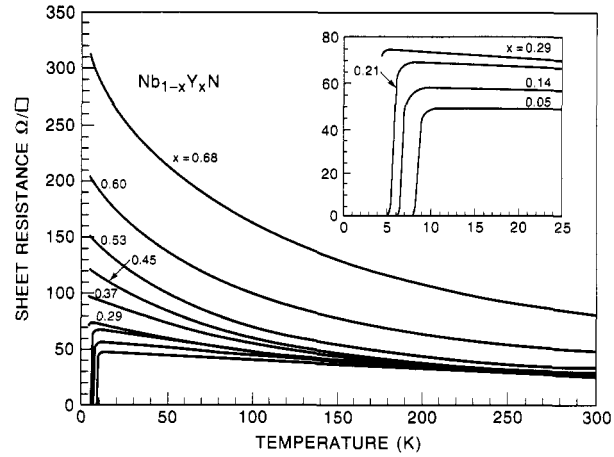

Figure 3. Temperature-dependent resistivity of the (Nb,Y)N films. The indicated compositions were inferred from lattice constants using Vegard's law. The inset shows the superconducting transitions for the four Nb-rich samples.

obtained in this cosputtering apparatus and allow us to infer that Figure 2 reflects the validity of Vegard's law (a_0 proportional to composition in a solid solution) and that the compositions shown range from Nb:Y = 32:68 to 95:5. Four-point resistivity measurements on the Nb–Y–N films (Figure 3) show a gradual decrease of the sheet resistance at a given temperature with increasing Nb content. Onset of superconductivity is observed close to 4.2 K when the Nb content approaches 71 metal atom %. The superconducting transition temperature T_c then gradually increases with increasing Nb content. This suggests that in this (Nb,Y)N solid solution the superconducting transition temperature can be continuously scaled from the T_c of pristine δ-NbN (14 K under present deposition conditions) to 4 K, and presumably below, by adjustment of the Y content. Note that (metallic) δ-NbN has an $R(T)$ curve which is essentially flat or has a slightly negative slope. This is commonly observed in NbN films and is attributed to a small grain size, which gives a very high scattering rate. This does not directly degrade superconductivity in the material (in fact, the small grain size leads to a high density of pinning sites, which results in extremely high critical currents in this material).

(Gd,Cr)N. An investigation of the Gd–Cr–N system was started by determining the conditions at which reactive sputtering of the elements individually produced cubic NaCl-type nitrides. The type of chromium nitride deposited proved to be highly sensitive to the composition and pressure of the sputtering gas. At 5 mTorr (0.67 Pa) of 15 mol % N_2/Ar (substrate temperature 750 °C) films of hexagonal β-Cr_2N[7] are formed (a = 4.776 (1) Å, c = 4.449 (2) Å by X-ray diffraction). The films exhibit a low resistivity (86 μΩ cm at 300 K) and metallic behavior. An increase of N_2 partial pressure to 30 mol % N_2/Ar and total pressure of 14.4 mTorr (1.9 Pa) results in deposition of films of cubic CrN (a = 4.135 (1) Å at 300 K), which are more resistive (ρ(300 K) = 1.87 mΩ cm). Resistivity measurements on this film show a marked inflection around the Neel temperature (approximately 270 K) reported for bulk samples.[8] Interestingly, in an earlier report on reactive rf sputtering of Cr–N films as function of N_2 partial pressure, only deposition of CrN and Cr metal

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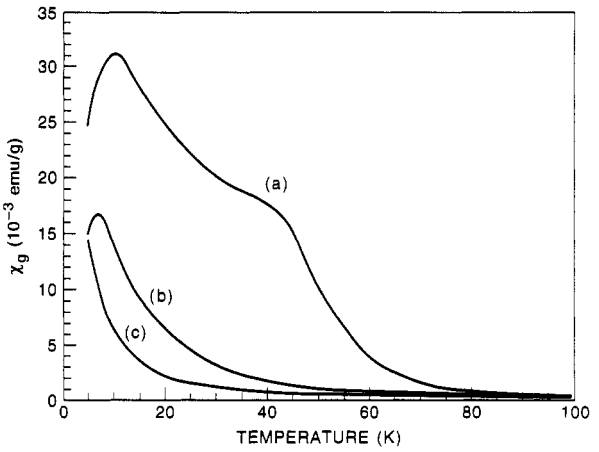

Figure 4. Magnetic susceptibility vs T for three Gd–Cr–N samples with increasing Cr content (from a to c), showing magnetic transitions of $Gd_{1-x}Cr_xN$ (in a) and (at lower temperatures) of the new Gd–Cr–N species.

was observed.[9] At both nitrogen partial pressures mentioned above, reactive sputtering of Gd produced films of cubic GdN (a = 4.990 (1) Å).[10] At 30 mol % N_2/Ar, the GdN produced had a magnetic transition at 30 K, below which the sample was ferromagnetic.

Reactive cosputtering of Gd and Cr at 30 mol % N_2/Ar (1.9 Pa total pressure, substrate temperature 750 °C) produced metallic gray specular films. They range in metal composition Cr:Gd from 90:10 to 37:63, as determined by Rutherford backscattering spectrometry. The average film thickness is 3000 Å. The films have a strongly negative temperature coefficient over the entire compositional range studied. The temperature dependence of the resistivity indicated that the samples are not in the intrinsic semiconducting regime, and thus an activation energy related to a band-gap cannot be inferred.[11] X-ray diffraction showed that the end members of the series of samples contained cubic NaCl-type nitrides with cell parameters differing slightly but reproducibly from the binaries. Cell parameters observed for the cubic Gd-rich and Cr-rich phases are respectively 4.960 (2) and 4.207 (2) Å. Assumption of Vegard's law for a cubic (Gd,Cr)N solid solution and the experimental cell parameters for the binary nitrides suggest solubility limits for this NaCl-type solid solution of $(Gd_{0.96}Cr_{0.04})N$ and $(Cr_{0.93}Gd_{0.07})N$ for the Gd- and Cr-rich side of the phase diagram, respectively. The X-ray diffraction lines get significantly broader on moving away from the Gd-rich or Cr-rich ends to more intermediate compositions, rendering X-ray diffraction useless for characterization of these samples. Electron microscopy showed that the grain size of the films deposited was very small (≤60 Å). Electron diffraction on a sample with (Cr:Gd) = (65:35) showed a powder ring pattern that is not derived from a NaCl-type structure.[12] It is accompanied by a trace of cubic $Gd_{1-x}Cr_xN$ phase, which is present more prominently in a Cr:Gd = 52:48 sample. The lines of the new species coexist with lines from cubic $Cr_{1-x}Gd_xN$ in a Cr:Gd = 77:23 sample.

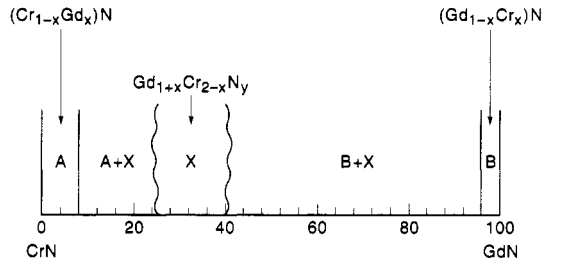

Figure 5. Tentative Gd–Cr–N compositional diagram deduced from the data on the Gd–Cr–N cosputtered films.

Magnetic susceptibility measurements on the films (Figure 4) showed the presence of two species in the Gd-rich samples that order magnetically. The transition at higher temperatures can be attributed to cubic $Gd_{1-x}Cr_xN$, the transition at lower temperatures appears to be due to the new species observed by electron diffraction: on increasing the Cr content the high-temperature transition recedes, whereas the low-temperature transition persists. This transition is initially found at 10 K and shifts to lower temperatures, eventually below 4 K at higher chromium content. Measurements of the paramagnetic susceptibility above 50 K indicate that the Gd and Cr moments are essentially constant for all of the samples. Assuming that the Gd^{3+} moment is ≈7.9 μ_B, the Cr effective moment is inferred to be ≈2.8 μ_B. This is somewhat lower than expected for Cr^{3+} and may indicate N deficiency. Measurements of the saturation moment were inconclusive, possibly due to complications associated with the extremely small grain size.

The data obtained thus far suggest the following for a tentative Gd–Cr–N phase diagram (Figure 5) under the applied conditions. At the Cr- and Gd-rich extremes of the Gd–Cr line, NaCl-type solid solutions $(Cr_{1-x}Gd_x)N$ ($x \leq 0.07$) and $(Gd_{1-x}Cr_x)N$ ($x \leq 0.04$) are found. Around the composition $Gd_{1/3}Cr_{2/3}$ a phase is present with a different structure type. This phase is probably not a line phase, as the magnetic transition temperature it exhibits varies with overall sample composition. The single-phase region of unknown width is flanked on either side of the composition line by mixed-phase regions where this phase coexists with either of the NaCl-type solid solution phases mentioned above. It should however be remembered that reactive sputtering deposition is a nonequilibrium process and that our findings summarized in Figure 5 do not represent phase relationships in thermodynamic equilibrium.

Summary and Conclusions

Reactive dc cosputtering of two metals is a convenient technique for preparation of M–M′–N thin films over a range of M–M′ compositions in a single run. Analysis of these films by RBS, X-ray diffraction, electron microscopy, and magnetic susceptibility and transport measurements has allowed an investigation of compound formation in the Nb–Y–N and Gd–Cr–N systems. We observed a new continuous (Nb,Y)N solid solution and found evidence for a new Gd–Cr–N species with a low-temperature magnetic transition. Although unsuitable to prepare bulk amounts of the ternary nitrides, the technique has allowed the study of two ternary nitride systems involving non-

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(11) The $R(T)$ curve of the most Gd-rich sample fits the form $R(T) = R_0e^{-a/T^{1/4}}$, indicating variable-range hopping. The other samples had a complicated temperature dependence which is not easily interpreted but certainly suggests some sort of activated process.

(12) Observed d spacings associated with the new species from electron diffraction are 2.91, 2.62, 2.30, 1.98, 1.40, 1.30, and 1.20 Å.

alloying metal pairs at substrate temperatures considerably lower than the usual annealing temperatures for ceramic nitrides. Furthermore, films that are extremely moisture sensitive can be protected from the atmosphere by a thin protective overlayer. This permits investigation of the electrical properties of the nitrides, which is often difficult or impossible to do with bulk air-sensitive powders. The information obtained by this cosputtering method may then be used to separately investigate specific compositions of interest (e.g., the Cr_2Gd metal ratio), for example, by sputter deposition of single-composition ternary nitride from an arc-molten and quenched mixed-metal target.